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FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER **215157US0XPCT** U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/926366
INTERNATIONAL APPLICATION NO. **PCT/EP00/03221**	INTERNATIONAL FILING DATE **11 APRIL 2000**	PRIORITY DATE CLAIMED **21 APRIL 1999**

TITLE OF INVENTION

RADIATION-CURABLE COMPOSITE LAYERED SHEET OR FILM

APPLICANT(S) FOR DO/EO/US

Rainer KOENIGER, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

    Request for Consideration of Documents in International Search Report
    Notice of Priority / PCT/IB/304 / PCT/IB/308
    Amended Sheets (pages 15 & 16)

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09/926366	PCT/EP00/03221	215157US0XPCT

24. The following fees are submitted:.

	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	16 - 20 =	0	x $18.00	**$0.00**	
Independent claims	2 - 3 =	0	x $84.00	**$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**$890.00**	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				**$0.00**	
SUBTOTAL =				**$890.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$0.00**	
TOTAL NATIONAL FEE =				**$890.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐				**$0.00**	
TOTAL FEES ENCLOSED =				**$890.00**	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of **$890.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. ________ in the amount of ________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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Surinder Sachar

SIGNATURE

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NAME

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REGISTRATION NUMBER

Oct. 22 2001

DATE

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215157US-0XPCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

RAINER KOENIGER ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW US PCT APPLN :
(Based on PCT/EP00/03221)

FILED: HEREWITH :

FOR: RADIATION-CURABLE COMPOSITE:
LAYERED SHEET OR FILM

09926366.102201

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

3. (Amended) The use of a sheet or film as claimed in claim 1, wherein there is additionally a coloring interlayer between the substrate layer and the outer layer.

4. (Amended) The use of a sheet or film as claimed in claim 1, wherein there is additionally a layer of polymethyl methacrylate between the coloring interlayer and the outer layer.

5. (Amended) The use of a sheet or film as claimed in claim 1, wherein the radiation-curable composition is in the noncrosslinked state.

6. (Amended) The use of a sheet or film as claimed in claim 1, wherein the radiation-curable composition comprises polymers containing ethylenically unsaturated groups, alone or as a mixture with low molecular mass, radiation-curable compounds, or mixtures of saturated, thermoplastic polymers with ethylenically unsaturated compounds.

7. (Amended) The use of a sheet or film as claimed in claim 1, wherein the substrate layer comprises a layer of thermoplastic polymers, particularly polymethyl methacrylates, polybutyl methacrylates, polyurethanes, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, polyamides, polycarbonates, acrylonitrile-butadiene-styrene (ABS) polymers, acrylic-styrene-acrylonitrile (ASA) copolymers, acrylonitrile-ethylene-propylene-diene-styrene copolymers (A-EPDM), polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

8. (Amended) A process for producing a radiation-curable composite layered sheet or film as claimed in claim 1, which comprises extruding the radiation-curable composition.

10. (Amended) A process for producing coated moldings, especially motor vehicle parts, which comprises adhesively bonding the radiation-curable composite layered sheet or film as claimed in claim 1 to said moldings and then curing the outer layer by means of radiation.

11. (Amended) A process for producing coated polymer moldings, especially motor vehicle parts, which comprises thermoforming a radiation-curable composite layered sheet or film as claimed in claim 1 in a thermoforming mold and injection-backmolding the reverse of

the substrate layer with the polymer composition, the radiation-curing of the outer layer taking place after the thermoforming operation or after injection backmolding.

12. (Amended) A coated molding obtainable by a process as claimed in claim 10.

15. (Amended) A sheet or film as claimed in claim 13, wherein the radiation-curable composition comprises polymers containing ethylenically unsaturated groups, alone or as a mixture with low molecular mass, radiation-curable compounds, or mixtures of saturated, thermoplastic polymers with ethylenically unsaturated compounds.

Please add the following new claim.

16. (New) A coated molding obtainable by a process as claimed in claim 10.

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REMARKS

Claims 1-16 are active in the present application. Claims 3-8, 10-12 and 15 have been amended to remove multiple dependencies. Claim 16 is a new claim. Support for new Claim 16 is found in original Claim 12. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

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Marked-Up Copy
Serial No:

Amendment Filed on:
10-22-01

IN THE CLAIMS

Please amend the claims as follows.

--3. (Amended) The use of a sheet or film as claimed in claim 1 [or 2], wherein there is additionally a coloring interlayer between the substrate layer and the outer layer.

4. (Amended) The use of a sheet or film as claimed in [any of claims 1 to 3] claim 1, wherein there is additionally a layer of polymethyl methacrylate between the coloring interlayer and the outer layer.

5. (Amended) The use of a sheet or film as claimed in [any of claims 1 to 4] claim 1, wherein the radiation-curable composition is in the noncrosslinked state.

6. (Amended) The use of a sheet or film as claimed in [any of claims 1 to 5] claim 1, wherein the radiation-curable composition comprises polymers containing ethylenically unsaturated groups, alone or as a mixture with low molecular mass, radiation-curable compounds, or mixtures of saturated, thermoplastic polymers with ethylenically unsaturated compounds.

7. (Amended) The use of a sheet or film as claimed in [any of claims 1 to 6] claim 1, wherein the substrate layer comprises a layer of thermoplastic polymers, particularly polymethyl methacrylates, polybutyl methacrylates, polyurethanes, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, polyamides, polycarbonates, acrylonitrile-butadiene-styrene (ABS)

polymers, acrylic-styrene-acrylonitrile (ASA) copolymers, acrylonitrile-ethylene-propylene-diene-styrene copolymers (A-EPDM), polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

8. (Amended) A process for producing a radiation-curable composite layered sheet or film as claimed in [any of claims 1 to 7] <u>claim 1</u>, which comprises extruding the radiation-curable composition.

10. (Amended) A process for producing coated moldings, especially motor vehicle parts, which comprises adhesively bonding the radiation-curable composite layered sheet or film as claimed in [any of claims 1 to 7] <u>claim 1</u> to said moldings and then curing the outer layer by means of radiation.

11. (Amended) A process for producing coated polymer moldings, especially motor vehicle parts, which comprises thermoforming a radiation-curable composite layered sheet or film as claimed in [any of claims 1 to 7] <u>claim 1</u> in a thermoforming mold and injection-backmolding the reverse of the substrate layer with the polymer composition, the radiation-curing of the outer layer taking place after the thermoforming operation or after injection backmolding.

12. (Amended) A coated molding obtainable by a process as claimed in claim 10 [or 11].

15. (Amended) A sheet or film as claimed in [either of claims 13 and 14] <u>claim 13</u>, wherein the radiation-curable composition comprises polymers containing ethylenically unsaturated groups, alone or as a mixture with low molecular mass, radiation-curable compounds, or mixtures of saturated, thermoplastic polymers with ethylenically unsaturated compounds.

16. (New)--

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Radiation-curable composite layered sheet or film

The invention relates to a radiation-curable composite layered sheet or film comprising at least one substrate layer and one outer layer, said outer layer being composed of a radiation-curable composition having a glass transition temperature of more than 40°C.

The specification further relates to a process for producing the radiation-curable composite layered sheet or film and to a process for producing moldings coated with said sheet or film.

DE-A-196 28 966 and DE-A-196 54 918 disclose dry-paint films where the paint has a glass transition temperature of less than 40°C. Curing requires two steps: a partial cure before the film is adhesively bonded to substrates, and the final cure thereafter.

EP-A-361 351 likewise discloses a dry-paint film. Here, the film is radiation-cured before being applied to the substrate moldings.

DE-A-196 51 350 (O.Z. 47587) describes composite layered sheets and films which consist of thermoplastic materials and do not have a radiation-curable coating.

A disadvantage of the radiation-curable dry-paint films known to date is that two or more steps are frequently required to effect the radiation cure, as described in DE-A-196 28 966. Where the film is fully radiation-cured prior to the coating operation, it often becomes brittle and difficult to deform, which is deleterious to its further processing.

With existing radiation-curable films, the coated moldings often lack sufficient scratch resistance and sufficient elasticity when worked on mechanically. It is an object of the present invention to provide radiation-curable composite layered sheets or films which are easy to process and which lend themselves to the coating of moldings by extremely simple techniques. The coated moldings are to have good mechanical properties, effective resistance to external influences, such as a good weathering stability, for example, and in particular are to be mechanically stable - having, for example, good scratch resistance and high elasticity.

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We have found that this object is achieved by the radiation-curable composite layered sheet or film defined at the outset and referred to for short as film hereinafter. We have also found processes for coating moldings with the film, and the coated moldings.

The film must include a substrate layer and an outer layer which is applied to the substrate layer directly or, where there are further interlayers, indirectly.

Outer layer

The outer layer is radiation-curable. Accordingly, the outer layer composition used is radiation-curable and comprises groups curable by a free-radical or ionic mechanism (curable groups for short). Preference is given to free-radically curable groups.

The radiation-curable composition is preferably transparent. After curing has been accomplished, as well, the outer layer is preferably transparent: that is, it is a clearcoat layer.

A key constituent of the radiation-curable compositions is the binder, which by filming forms the outer layer.

The radiation-curable composition preferably comprises a binder selected from

i) polymers containing ethylenically unsaturated groups

ii) mixtures of i) with ethylenically unsaturated compounds of low molecular mass

iii) mixtures of saturated thermoplastic polymers with ethylenically unsaturated compounds.

i)

Examples of suitable polymers include those of ethylenically unsaturated compounds, but also polyesters, polyethers, polycarbonates, polyepoxides or polyurethanes.

They suitably include unsaturated polyester resins, which consist essentially of polyols, especially diols, and polycarboxylic acid, especially dicarboxylic acid, where one of the esterification components contains a copolymerizable,

ethylenically unsaturated group. Examples of the components in question include maleic acid, fumaric acid, and maleic anhydride.

Preference is given to polymers of ethylenically unsaturated compounds, such as are obtained in particular by means of free-radical addition polymerization.

The free-radical addition polymers include, in particular, polymers composed of more than 40% by weight, with particular preference more than 60% by weight, of acrylic monomers, particularly C_1-C_8, preferably C_1-C_4, alkyl (meth)acrylates. By way of ethylenically unsaturated groups, the polymers include in particular (meth)acrylic groups. These groups may be attached to the polymer by, for example, reacting (meth)acrylic acid with epoxide groups in the polymer (e.g., by using glycidyl (meth)acrylate as a comonomer).

Preference is likewise given to polyurethanes. Their unsaturated groups are again preferably (meth)acrylic groups, attached to the polyurethane by reacting hydroxyalkyl (meth)acrylates with isocyanate groups, for example.

The polymers i) per se can be processed as thermoplastics.

ii)

The unsaturated polymers i) may also be used in mixtures with ethylenically unsaturated compounds of low molecular mass.

Low molecular mass compounds in this context are compounds having a number average molecular weight of less than 2000 g/mol (as determined by gel permeation chromatography using a polystyrene standard).

Suitable examples include free-radically polymerizable compounds containing only one ethylenically unsaturated, copolymerizable group.

By way of example, mention may be made of C_1-C_{20} alkyl (meth)acrylates, vinylaromatics having up to 20 carbon atoms, vinyl esters of carboxylic acids containing up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl ethers of alcohols containing from 1 to 10 carbon atoms, and aliphatic hydrocarbons having from 2 to 20, preferably from 2 to 8, carbon atoms and 1 or 2 double bonds.

Preferred alkyl (meth)acrylates are those with a C_1–C_{10} alkyl radical, such as methyl methacrylate, methyl acrylate, n-butyl acrylate, ethyl acrylate and 2-ethylhexyl acrylate.

Also suitable, in particular, are mixtures of the alkyl (meth)acrylates.

Examples of vinyl esters of carboxylic acids having from 1 to 20 carbon atoms are vinyl laurate, vinyl stearate, vinyl propionate, and vinyl acetate.

Examples of suitable vinylaromatic compounds are vinyltoluene, α-butylstyrene, 4-n-butylstyrene, 4-n-decylstyrene, and preferably styrene.

Examples of nitriles are acrylonitrile and methacrylonitrile.

Examples of suitable vinyl ethers are vinyl methyl ether, vinyl isobutyl ether, vinyl hexyl ether, and vinyl octyl ether.

As nonaromatic hydrocarbons having from 2 to 20, preferably from 2 to 8, carbon atoms and one or two olefinic double bonds, mention may be made of butadiene, isoprene, and also ethylene, propylene, and isobutylene.

Compounds contemplated include preferably free-radically polymerizable compounds containing two or more ethylenically unsaturated groups.

The compounds in question are particularly (meth)acrylate compounds, with preference being given in each case to the acrylate compounds: i.e., the derivatives of acrylic acid.

Preferred (meth)acrylate compounds contain from 2 to 20, more preferably from 2 to 10, and with very particular preference from 2 to 6, copolymerizable, ethylenically unsaturated double bonds.

As (meth)acrylate compounds mention may be made of (meth)acrylates and in particular acrylates of polyfunctional alcohols, especially those which contain no functional groups other than the hydroxyl groups or, if having further functional groups, contain only ether groups. Examples of such alcohols include difunctional alcohols, such as ethylene glycol and propylene glycol, and their higher condensation analogs, such as diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, etc., butanediol, pentanediol, hexanediol, neopentyl glycol, alkoxylated phenolic compounds, such as

ethoxylated and/or propoxylated bisphenols, cyclohexanedimethanol, alcohols with a functionality of three or more, such as glycerol, trimethylolpropane, butanetriol, trimethylolethane, pentaerythritol, dimethylolpropane, dipentaerythritol, sorbitol, mannitol, and the corresponding alkoxylated alcohols, especially ethoxylated and propoxylated alcohols.

The alkoxylation products are obtainable conventionally by reacting the above alcohols with alkylene oxides, especially ethylene oxide or propylene oxide. With preference the degree of alkoxylation per hydroxyl group is from 0 to 10, i.e., 1 mol of hydroxyl group may be alkoxylated preferably with up to 10 mol of alkylene oxides.

(Meth)acrylate compounds further include polyester (meth)acrylates, which are the (meth)acrylic esters of polyesterols.

Examples of suitable polyesterols are those such as may be prepared by esterifying polycarboxylic acids, preferably dicarboxylic acids, with polyols, preferably diols. The starting materials for such hydroxyl-containing polyesters are known to the skilled worker. As dicarboxylic acids preferential use may be made of succinic acid, glutaric acid, adipic acid, sebacic acid, o-phthalic acid, their isomers and hydrogenation products, and also esterifiable derivatives, such as anhydrides or dialkyl esters of said acids. Suitable polyols include the abovementioned alcohols, preferably ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, and cyclohexanedimethanol, and also polyglycols of the ethylene glycol and propylene glycol types.

Polyester (meth)acrylates may be prepared in a plurality of stages or else in a single stage, as described, for example, in EP 279 303, from acrylic acid, polycarboxylic acid, and polyol.

iii)
Examples of suitable saturated thermoplastic polymers include polymethyl methacrylate, polystyrene, high-impact polymethyl methacrylate, high-impact polystyrene, polycarbonate and polyurethanes.

Radiation-curability is ensured by adding an ethylenically unsaturated, radiation-curable compound. This may be one of the compounds listed under i) and/or ii).

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A key feature of the binder i) to iii) is that its glass transition temperature (Tg) is more than 40°C, preferably more than 50°C, and with particular preference more than 60°C. In general, the Tg will not exceed a level of 130°C. (The figures relate to the binder before radiation curing.)

The glass transition temperature, Tg, of the binder may be determined by the DSC (differential scanning calorimetry) method in accordance with ASTM 3418/82.

The amount of the curable groups, i.e., the ethylenically unsaturated groups, is preferably from 0.001 to 0.2 mol, with particular preference from 0.005 to 0.15 mol, with very particular preference from 0.01 to 0.1 mol, per 100 g of binder (solids; that is, without water or other solvents).

The binder preferably has a viscosity of from 0.02 to 100 Pas at 140°C (as determined in a rotational viscometer).

The radiation-curable compositions may include further constituents. Particular mention may be made of photoinitiators, leveling agents, and stabilizers. For outdoor use, i.e., for coatings directly exposed to daylight, the compositions will particularly include UV absorbers and free-radical scavengers.

UV absorbers convert UV radiation into heat energy. Known UV absorbers include hydroxybenzophenones, benzotriazoles, cinnamic esters, and oxalanilides.

Free-radical scavengers bind free-radical intermediates that are formed. Major free-radical scavengers include sterically hindered amines, known as HALS (hindered amine light stabilizers).

For outdoor applications, the overall UV absorber and free-radical scavenger content is preferably from 0.1 to 5 parts by weight, with particular preference from 0.5 to 4 parts by weight, based on 100 parts by weight of the radiation-curable compounds.

Moreover, besides radiation-curable compounds, the radiation-curable composition may further include compounds which contribute to curing by other chemical reactions. Suitable examples include polyisocyanates, which crosslink with hydroxyl or amino groups.

The radiation-curable composition may be in water-free and solvent-free form, or in the form of a solution or dispersion.

Preference is given to water- and solvent-free radiation-curable compositions, or aqueous solutions or aqueous dispersions.

Particular preference is given to water- and solvent-free radiation-curable compositions.

The radiation-curable composition is thermoplastically deformable and in particular may be extruded.

The above radiation-curable compositions form the outer layer. The layer thickness (after drying and curing) is preferably from 10 to 100 µm.

Substrate layer

The substrate layer serves as a support and is intended to ensure that the composite as a whole remains permanently tough.

The substrate layer consists preferably of a thermoplastic polymer, particularly polymethyl methacrylates, polybutyl methacrylates, polyurethanes, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, polyamides, polycarbonates (PC), acrylonitrile-butadiene-styrene (ABS) polymers, acrylic-styrene-acrylonitrile (ASA) copolymers, acrylonitrile-ethylene-propylene-diene-styrene copolymers (A-EPDM), polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

Preference is given to ASA, especially in accordance with DE 19 651 350, and to the ASA/PC blend. Preference is likewise given to polymethyl methacrylate (PMMA) or impact-modified PMMA.

The layer thickness is preferably from 50 µm up to 5 mm. Particular preference, especially when the substrate layer is injection-backmolded, is given to thicknesses of from 100 to 1000 µm, in particular from 100 to 500 µm.

The polymer of the substrate layer may comprise additives, especially fillers or fibers. The substrate layer may also be colored, in which case it may also act as a coloring layer.

Further layers

The film may include further layers in addition to the outer layer and the substrate layer.

Suitable examples include coloring interlayers or further layers of thermoplastic material (thermoplastic interlayers), which strengthen the film or serve as release layers.

Thermoplastic interlayers may be made of the polymers listed above under Substrate layer.

Particular preference is given to polymethyl methacrylate (PMMA), preferably impact-modified PMMA. Mention may also be made of polyurethane. Coloring layers may likewise consist of said polymers. They include dyes or pigments which are distributed in the polymer layer.

One preferred film has, for example, the following layer structure, the alphabetical sequence corresponding to the spatial disposition:

A) outer layer
B) thermoplastic interlayer (optional)
C) coloring interlayer (optional)
D) substrate layer
E) adhesive layer (optional)

On the reverse side (reverse for short) of the substrate layer (i.e., the side facing the article to be coated) there may have been applied an adhesive layer, where the film is to be bonded adhesively to the substrate.

Applied to the transparent outer layer there may be a protective layer, e.g., a removable film, which prevents unintended curing. Its thickness may amount, for example, to from 50 to 100 µm. The protective layer may be composed, for example, of polyethylene or polyterephthalate. The protective layer may be removed prior to irradiation.

Alternatively, irradiation may take place through the protective layer; for this, the protective layer must be transparent in the irradiation wavelength range.

The overall thickness of the film is preferably from 50 to 1000 µm.

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Production of the composite sheet or film

The production of a composite from the layers B) to D) may take place, for example, by coextrusion of all or some of the layers.

For coextrusion, the individual components are fluidified in extruders and, using special means, are contacted with one another in such a way as to give the films having the layer sequence described above. For example, the components may be coextruded through a slot die. This process is elucidated in EP-A2-0 225 500. As a supplement to the processes described herein, it is also possible to use the process known as adapter coextrusion.

The composite may be produced by conventional processes, for example, by coextrusion, as described above, or by lamination of the layers, in a heatable nip, for example. In this way it is possible first of all the produce a composite of the layers except for the outer layer, and then to apply the outer layer by conventional techniques.

The radiation-curable composition may be applied to the substrate layer or the composite in a simple way, by casting, rolling, knife coating, spraying, etc., for example, and dried where appropriate.

Preference is given to extruding the radiation-curable composition, i.e., the outer layer. Where appropriate, the radiation-curable composition may also be coextruded with one or more further layers.

In the case of extrusion (including coextrusion) of the radiation-curable compositions, the preparation of the radiation-curable composition by mixing of its constituents, and the preparation of the outer layer, may take place in one operation.

To this end, thermoplastic constituents, e.g., unsaturated polymers i) or saturated polymers iii) (see above), may first of all be melted in the extruder. The requisite melting temperature depends on the polymer in question. After the melting operation, preferably, the further constituents may be metered in, especially radiation-curable compounds ii) of low molecular mass (see above). The compounds act as plasticizers, thereby reducing the temperature at which the composition is in melt form. The temperature on addition of the radiation-curable compound must

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lie in particular below a critical temperature at which the radiation-curable compound undergoes thermal curing.

The critical temperature may easily be determined by means of a calorimetric measurement, i.e., a measurement of the heat absorbed with increasing temperature, in accordance with the above-described determination of the glass transition temperature.

The radiation-curable composition is then extruded directly as the outer layer onto the existing composite or, in the case of coextrusion, is extruded with layers of the composite. Extrusion leads directly to the composite layered sheet or film.

The outer layer is blocking-resistant, i.e., does not adhere, and is radiation-crosslinkable. The composite sheet or film is thermoelastically deformable. If desired, a protective layer (protective film) may be laid down on the outer layer directly following production of the composite sheet or film.

The composite layered sheet or film possesses high gloss and good mechanical properties. Rarely is cracking observed.

The extensibility of the composite layered sheet or film is preferably at least 100%, relative to the unextended state (at 140°C, with a thickness of 30 μm).

Use processes

The film may be stored without partial curing (as described in DE-A-19 628 966) until subsequent use.

There is very little, if any, sticking or deterioration in performance properties observed up until the time of subsequent use.
The film is used preferably as a coating material.

In this case, a preferred procedure is first to coat the substrates and then to cure the outer layer by means of radiation.

Coating may take place by bonding the film to the substrates. For this purpose, on the reverse of the substrate layer, the film is preferably provided with the adhesive layer E. Suitable substrates include those of wood, plastic or metal.

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Coating may also take place by injection backmolding of the film. For this purpose the film is thermoformed, preferably in a thermoforming mold, and the reverse of the substrate layer is injection-backmolded with polymer composition. The polymer composition comprises, for example, polymers which were listed above in the description of the substrate layer or, for example, polyurethane, especially polyurethane foam. The polymers may comprise additives, particular examples including fibers, such as glass fibers, or fillers.

The radiation curing of the outer layer takes place in this case preferably after the thermoforming operation and with particular preference after the injection backmolding of the film.

The radiation cure is effected with high-energy light, e.g., UV light, or electron beams. It may take place at relatively high temperatures. Preference is given here to a temperature above the Tg of the radiation-curable binder.

Where crosslinkers which bring about additional thermal crosslinking, such as isocyanates, have been included too, it is possible to carry out thermal crosslinking by raising the temperature to up to 150°C, preferably up to 130°C, which can be done, for example, simultaneously with or else subsequent to radiation curing.

Applications and advantages

The films may be used to coat shaped articles. Any desired shaped articles are amenable. With particular preference, the films are used to coat shaped articles where very good surface properties, high weathering stability, and good UV resistance are important. The resulting surfaces are, moreover, highly scratch-resistant and firmly adhering, thereby reliably preventing destruction of the surfaces by scratching or delamination of the surfaces. Accordingly, shaped articles for use outdoors, outside of buildings, constitute a preferred area of application. In particular, the films are used to coat motor vehicle parts, with suitable examples including wings, door trim components, fenders, spoilers, skirts, and exterior mirrors.

Examples:

I Synthesis of a radiation-curable coating material:

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426.2 g of isopropylidenedicyclohexanol were dispersed roughly in 566.3 g of hydroxyethyl acrylate at 60°C with stirring. To this dispersion there were added 1695.2 g of an isocyanurate of hexamethylene diisocyanate, 1.34 g of hydroquinone monomethyl ether, 2.69 g of 1,6-di-tert-butyl-para-cresol and 0.134 g of phenothiazine. Following the addition of 0.538 g of dibutyltin dilaurate, the batch heated up to 93°C over the course of 20 minutes. After it had been cooled to 75°C, 300 g of acetone were metered in. When the NCO value had dropped to 0.66%, a further 370 g of acetone were added, followed by dropwise addition of 14.87 g of methanol. The mixture was then stirred at 60°C until the NCO value had fallen to 0. The resin was admixed with an appropriate photoinitiator, applied to a Luran S 797 injection backmolding film, and exposed at 100°C. The pencil hardness of the films was determined in accordance with ASTM D 3363.
Pencil hardness of the coated film: 2H

Comparison: pencil hardness of the untreated injection backmolding film (Luran S 797): B

Comparison: pencil hardness of the injection-backmolding protection film (Lucryl G 87): softer than 6B

Two uncured acrylated polyacrylates having different Tg values, and the uncured urethane acrylate, were applied to a Luran S support film and thermoformed at an elevated temperature. After thermoforming, the films were exposed at 100°C.

Hardness of the films:

Urethane acrylate	2H
Binder resin (Tg (before exposure)=46°C)	3H
Binder resin (Tg (before exposure)=-6°C)	H

II Production of a radiation-curable outer layer

IIa

First of all, a photoactive mixture was prepared by mixing the following constituents:

Material	% by weight	chemical composition
Ebecryl® 40	23	Alkoxylated pentaerythritol triacrylate (UCB)
Ebecryl® IRR 264	41	Triacrylate of a tris(2-hydroxyethyl) isocyanurate (UCB)

Ebecryl® 1290	11	Aliphatic urethane acrylate (UCB)
Ebecryl® 5129	11	Aliphatic urethane acrylate (UCB)
Ebecryl® 350	5	Silicone diacrylate (UCB)
Tinuvin® 292	1	HALS additive (Ciba SC)
Tinuvin® 400	1	UV absorber (Ciba SC)
Irgacure® 184	6	Photoinitiator (Ciba SC)
Lucirin® TPO	1	Photoinitiator (BASF)

The polymethyl methacrylate (PMMA) Lucryl® G 55 was melted at from 190 to 220°C in an extruder and the photoactive mixture (one part by weight of the mixture to three parts by weight of Lucryl) was metered into the melt at below 170°C. The resulting melt was extruded in the form of a radiation-curable film.

The film obtained was blocking-resistant (i.e., nonadhering) and the resulting composite film was deformable and thermoformable. The radiation-curable outer layer was cured using UV light. (120 W/cm, belt speed 2 to 3 m/min).

IIb

The photoactive mixture consisted of:

Material	% by weight	chemical mixture
Ebecryl 2000	43	Aliphatic urethane acrylate (UCB)
Ebecryl 264	22	Aliphatic triacrylate of a urethane acrylate in HDDA (UCB)
Lucirin TPO-L	1	Photoinitiator (BASF)
CGI 184	5	Photoinitiator (Ciba SC)
Tinuvin 292	2	HALS additive (Ciba SC)
Tinuvin 400	2	UV absorber (Ciba SC)
SR 9003	7	Propoxylated neopentyl glycol diacrylate (Cray Valley)
Ebecryl 350	2	Silicone diacrylate (UCB)
CN 965	10	Aliphatic UR-Ac (Cray Valley)
SR 344	5	Polyethylene glycol diacrylate (Cray Valley)

The polyurethane KU-1-8602 (Bayer) was melted at 180 to 220°C in an extruder and the photoactive mixture (one part by weight to three parts by weight of polyurethane) was metered into the melt at 160°C. The resulting melt was extruded in the form of a radiation-curable film.

The resulting outer layer was blocking-resistant, and the resulting film was deformable and thermoformable.

The radiation-curable outer layer was cured using UV light (120 W/cm, belt speed 2 to 3 m/min).

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ART 34 AMDT

New claims:

1. The use of a radiation-curable composite layered sheet or film comprising at least one substrate layer and one outer layer for coating moldings, wherein the outer layer is composed of a radiation-curable composition which comprises a binder having a glass transition temperature of more than 40°C.

2. The use of a sheet or film as claimed in claim 1, wherein the outer layer is transparent.

3. The use of a sheet or film as claimed in claim 1 or 2, wherein there is additionally a coloring interlayer between the substrate layer and the outer layer.

4. The use of a sheet or film as claimed in any of claims 1 to 3, wherein there is additionally a layer of polymethyl methacrylate between the coloring interlayer and the outer layer.

5. The use of a sheet or film as claimed in any of claims 1 to 4, wherein the radiation-curable composition is in the noncrosslinked state.

6. The use of a sheet or film as claimed in any of claims 1 to 5, wherein the radiation-curable composition comprises polymers containing ethylenically unsaturated groups, alone or as a mixture with low molecular mass, radiation-curable compounds, or mixtures of saturated, thermoplastic polymers with ethylenically unsaturated compounds.

7. The use of a sheet or film as claimed in any of claims 1 to 6, wherein the substrate layer comprises a layer of thermoplastic polymers, particularly polymethyl methacrylates, polybutyl methacrylates, polyurethanes, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, polyamides, polycarbonates, acrylonitrile-butadiene-styrene (ABS) polymers, acrylic-styrene-acrylonitrile (ASA) copolymers, acrylonitrile-ethylene-propylene-diene-styrene copolymers (A–EPDM), polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

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8. A process for producing a radiation-curable composite layered sheet or film as claimed in any of claims 1 to 7, which comprises extruding the radiation-curable composition.

9. A process as claimed in claim 8, wherein the radiation-curable composition and at least one further layer are coextruded.

10. A process for producing coated moldings, especially motor vehicle parts, which comprises adhesively bonding the radiation-curable composite layered sheet or film as claimed in any of claims 1 to 7 to said moldings and then curing the outer layer by means of radiation.

11. A process for producing coated polymer moldings, especially motor vehicle parts, which comprises thermoforming a radiation-curable composite layered sheet or film as claimed in any of claims 1 to 7 in a thermoforming mold and injection-backmolding the reverse of the substrate layer with the polymer composition, the radiation-curing of the outer layer taking place after the thermoforming operation or after injection backmolding.

12. A coated molding obtainable by a process as claimed in claim 10 or 11.

13. A sheet or film comprising at least one substrate layer and one outer layer composed of a radiation-curable composition which comprises a binder having a glass transition temperature of more than 40°C, wherein there is additionally a coloring interlayer between the substrate layer and the outer layer.

14. A sheet or film as claimed in claim 13, wherein there is additionally a layer of polymethyl methacrylate between the coloring interlayer and the outer layer.

15. A sheet or film as claimed in either of claims 13 and 14, wherein the radiation-curable composition comprises polymers containing ethylenically unsaturated groups, alone or as a mixture with low molecular mass, radiation-curable compounds, or mixtures of saturated, thermoplastic polymers with ethylenically unsaturated compounds.

Radiation-curable composite layered sheet or film

Abstract

A radiation-curable composite layered sheet or film comprising at least one substrate layer and one outer layer, said outer layer being composed of a radiation-curable composition having a glass transition temperature of more than 40°C.

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Declaration, Power of Attorney

0050/049913

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Radiation-curable composite layered sheet or film

the specification of which

[ ] is attached hereto.

[ ] was filed on ______________________ as

Application Serial No. ______________________

and amended on ______________________.

[x] was filed as PCT international application

Number PCT/EP00/03221

on 11/04/00

and was amended under PCT Article 19

on ______________________ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above–identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	**Country**	**Day/Month/Year**	**Priority Claimed**
19917965.4	*Germany*	*21 April 1999*	[x] Yes [ ] No

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We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
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We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	**Filing Date**	**Status (pending, patented, abandoned)**

And we (I) hereby appoint:

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Robert W. Hahl, Registration Number 33, 893, our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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